Thermodynamic Properties of Ar$_3$[1]

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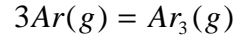_____

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ABSTRACT

Using a cluster approach to the statistical thermodynamics of ideal gases, it can be shown that for the reaction

$$3Ar(g) = Ar_3(g)$$

The partition function, q, of the Ar_3 molecule can be written as

$$q(Ar_3) - \frac{kT}{2P}\left(\frac{2\pi m_{Ar}kT}{h^2}\right)^{9/2} e^{-3\varepsilon_{0,el}/kT} C(T)$$

and the heat capacity is given by

$$C_p^{\,o}(Ar_3) = R\left[\frac{11}{2} + 2T\frac{dC(T)/dT}{C(T)} + T^2\frac{d^2C(T)/dT^2}{C(T)} - T^2\left(\frac{dC(T)/dT}{C(T)}\right)^2\right]$$

where C(T) is the third virial coefficient for the system. Accurate two body and three body interaction potentials have been determined for Ar_3 and have been used to calculate C(T). These previous results are used in this paper to calculate $C_p^{\,o}(Ar_3)$ as a function of temperature, using the cluster approach to statistical thermodynamics.

Also, geometric models of the Ar_3 molecule are available and these models have been used in this paper to calculate $C_p^{\,o}(Ar_3)$ as a function of temperature by the more common statistical mechanical approach; directly in terms of the partition function. Results obtained using the two methods are compared.

KEY WORDS: argon trimer; heat capacity; partition function; third virial coefficient.

1. INTRODUCTION

This paper presents theoretical calculations of the heat capacity of Ar_3 from 200K to 5000K. Two methods are used; the usual statistical mechanical method involving the evaluation of partition functions and a cluster approach that leads to expressions for the thermodynamic properties of Ar_3 in terms of the third virial coefficient and its derivatives. Results obtained using the two methods are in reasonable agreement although they differ in details.

2. THE PARTITION FUNCTION APPROACH

The usual way in which the thermodynamic properties of gas phase molecules are calculated is by using the partition function [1]. For 1 mol of an ideal gas, the partition function, Q, is written as

$$Q = \frac{1}{No!}(q_{tr}q_{el}q_{in})^{No}$$

where No is Avogadro's number and the q's signify contributions to the partition function of a single molecule from the translational, electronic, and internal degrees of freedom. Also

$$q_{in} = q_{vib}q_{rot}q_{cor}$$

where q_{vib} is the contribution to the internal partition function from harmonic vibration, q_{rot} is the contribution to the internal partition function from rigid rotation, and q_{cor} is the "correction" to the internal partition function due to anharmonic vibration, non-rigid rotation (e.g. centrifugal stretching) and other effects such as the coupling of vibration and rotation.

The Ar_3 molecule will be assumed to be in its ground electronic state. Experimental spectroscopic constants are not available for this molecule for use in evaluating the partition functions since Ar_3 has no dipole moment and no infrared spectrum. The theoretical model for this molecule in its most stable configuration indicates that it is essentially an equilateral triangle [2,3,4] with an Ar atom at each apex; there may also be small contributions from other configurations [4].

The theoretical rotational constant, B_e, of Ar_3 in the ground vibrational state [2] is 0.0573 cm^{-1} with slightly different results obtained for the molecule in excited vibrational states. This molecule has three vibrational modes with [2] frequencies $\omega_{e,1} = 22.77$ cm^{-1} for the $(0,0,0) \rightarrow (0,0,1)$ transition, $\omega_{e,2} = 23.04$ cm^{-1} for the $(0,0,0) \rightarrow (0,1,0)$ transition, and $\omega_{e,3} = 32.92$ cm^{-1} for the $(0,0,0) \rightarrow (1,0,0)$ vibrational transition. Somewhat different frequencies are obtained for vibrational excitations to more highly excited states. Thus there is an anharmonicity effect but it will be ignored for these calculations since the effect of anharmonicity and other "corrections" on the thermodynamic properties is usually very small. Thus q_{cor} is taken to be unity for these calculations and, with the zero of energy taken to be Ar_3 in its most stable configuration in the ground electronic state,

$$Q = \frac{1}{No!}(q_{tr}q_{vib}q_{rot})^{No}$$

A standard result [1] for the statistical mechanics of gas phase molecules is

$$H_T^o - H_0^o = RT^2\left(\frac{\partial LnQ}{\partial T}\right)_{N,V} + RT$$

where H_T^o is the standard enthalpy at temperature T and H_0^o is the standard enthalpy at 0K. Also

$$C_p^o = \left(\frac{\partial (H_T^o - H_0^o)}{\partial T} \right)_p$$

where C_p^o is the standard heat capacity at constant pressure. For Ar_3, B_e is small and the rotational degrees of freedom can be considered to be fully excited. Thus the result is

$$C_p^o = 4R + R\left[\left(\frac{hc\omega_{e,1}/kT}{e^{-hc\omega_{e,1}/kT} - 1} \right)^2 + \left(\frac{hc\omega_{e,2}/kT}{e^{-hc\omega_{e,2}/kT} - 1} \right)^2 + \left(\frac{hc\omega_{e,3}/kT}{e^{-hc\omega_{e,3}/kT} - 1} \right)^2 \right]$$

Results are shown in the second column of Table I. Since the vibrational frequencies are low, vibration is nearly fully excited, even at low temperatures, and C_p^o approaches its classical value; i.e. $C_p^o = 7R = 58.20$ J/mol/K, at all temperatures considered in these calculations.

3. THE CLUSTER APPROACH

An alternative way to approach the statistical mechanical calculation of the thermo-dynamic properties of ideal gases is to consider the reaction in which a gas atom, X, forms a cluster of n atoms; i.e.

$$nX(g) = X_n(g)$$
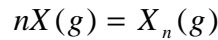
The relation of this equilibrium reaction to the virial coefficients has been considered in detail [1,5-15]. The reaction of interest in this paper is

$$3Ar(g) = Ar_3(g)$$
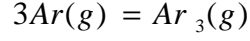
For this reaction

$$K_c^{\,o} = \frac{C(Ar_3)/C^o}{C(Ar)^3/(C^o)^3} = \frac{(NoVC^o)^2 N_{Ar3}}{N_{Ar}^{\,3}}$$

where $K_c^{\,o}$ is the standard equilibrium constant in terms of concentration, C (in mol/liter), $C^o = 1$ mol/liter, N_{ar} and N_{Ar3} are the number of Ar atoms and the number of Ar_3 molecules, respectively, in the container and V is the volume of the container. The species are assumed to be ideal gases. The equation above can be rewritten as

$$N_{Ar3} = \frac{K_c^{\,o}}{(C^oVNo)^2} N_{Ar}^{\,3}$$

Let [5]

$$N = \text{total number of Ar atoms} = N_{Ar} + 3N_{Ar3}$$

or

$$N_{Ar} = N - 3N_{Ar3}$$

For a mixture of the ideal gases Ar and Ar_3

$$\frac{P}{RT} = \frac{P}{NokT} = \frac{n}{V} = \frac{n_{Ar} + n_{Ar3}}{V} = \frac{N_{Ar} + N_{Ar3}}{NoV}$$

where n denotes the number of mols. This can be written as

$$\frac{P}{kT} = \frac{N_{Ar} + N_{Ar3}}{V} = \frac{N}{V} - \frac{2N_{Ar3}}{V}$$

Upon substituting for N_{Ar3}, this becomes

$$\frac{P}{kT} = \frac{N}{V} - \frac{2K_c^{\,o}}{(C^o No)^2 V^3}(N^3 - 6N^2 N_{Ar3} + 18NN_{Ar3}^{\;2} - 27N_{Ar3}^{\;3})$$

Upon continuing to substitute for N_{Ar3}, the result

$$\frac{P}{kT} = \frac{N}{V} - \frac{2K_c^{\,o}}{(C^o No)^2}\frac{N^3}{V^3} + O\!\left(\frac{N^5}{V^5}\right) + O\!\left(\frac{N^7}{V^7}\right) + O\!\left(\frac{N^9}{V^9}\right) + \ldots$$

is obtained. The virial equation of state is

$$\frac{P}{kT} = \frac{N}{V} + \frac{B(T)}{No}\frac{N^2}{V^2} + \frac{C(T)}{No^2}\frac{N^3}{V^3} + \frac{D(T)}{No^3}\frac{N^4}{V^4} + \ldots$$

where B(T), C(T), D(T), etc. are the second, third, fourth, etc. virial coefficients. Upon comparing the last two equations, the result

$$C(T) = -\frac{2}{(C^o)^2}K_c^{\,o}$$

is obtained. This is not the same result found in reference [6]. However, Wooley considers a mixture of the clusters X, X_2, X_3, X_4, etc. In this paper, only the clusters Ar and Ar_3 are allowed. If K_c is taken to be the equilibrium constant in terms of the ratios of concentrations; i.e. for this reaction

$$K_c = \frac{C_{Ar3}}{(C_{Ar})^3}$$

then the last equation can be written as

$$K_c = -\frac{C(T)}{2}$$

Now, K_c can be written [10] in terms of the partition functions for these species; i.e.

$$K_c = \frac{q(Ar_3)/V}{\left(q(Ar)/V\right)^3} = -\frac{C(T)}{2}$$

or

$$q(Ar_3) = -\frac{C(T)}{2V^2}q(Ar)^3 = -\frac{C(T)}{2V^2}\left[q_{tr}(Ar)q_{el}(Ar)\right]^3$$

The nuclear spin partition functions of the atom and molecule have been ignored since, assuming the nuclei behave independently, these partition functions cancel [1] in the last equation. Using the ideal gas law and the explicit result for $q_{tr}(Ar)$, the result

$$q(Ar_3) = -\frac{C(T)}{2}\frac{kT}{P}\left(\frac{2\pi m_{Ar}kT}{h^2}\right)^{9/2}q_{el}(Ar)^3$$

is obtained.

For 1 mol of Ar_3 molecules

$$H_T^o - H_0^o = RT^2\left(\frac{\partial Lnq(Ar_3)}{\partial T}\right)_P = RT\left[\frac{11}{2}+T\frac{dC(T)/dT}{C(T)}+\frac{3\varepsilon_{o.el}}{kT}\right]$$

where the expression

$$q_{el}(Ar) = e^{-\varepsilon_{o,el}kT}$$

has been used. The result for the enthalpy depends on the third virial coefficient, $C(T)$, its first derivative, and the electronic energy of an Ar atom in the ground state, $\varepsilon_{0,el}$, deter-

mined relative to the ground state of Ar_3. It is common to write these results in terms of reduced variables; i.e.

$$C^*(T^*) = \frac{C(T)}{b_o^{\,2}} \qquad\qquad T^* = \frac{kT}{\varepsilon_{0,el}} \qquad\qquad C_1^{\;*}(T^*) = T^* \frac{dC^*(T^*)}{dT^*}$$

where

$$b_o = \frac{2}{3}\pi\sigma^3$$

and σ is the effective rigid sphere diameter of the interacting atoms. The expression for the enthalpy can be written as

$$H_T^{\;o} - H_0^{\;o} = RT\left[\frac{11}{2} + \frac{C_1^{\;*}(T^*)}{C^*(T^*)} + \frac{3\varepsilon_{o.el}}{kT}\right]$$

in reduced variables. Also

$$C_p^{\;o} = R\left[\frac{11}{2} + 2\frac{C_1^{\;*}(T^*)}{C^*(T^*)} + \frac{C_2^{\;*}(T^*)}{C^*(T^*)} - \left(\frac{C_1^{\;*}(T^*)}{C^*(T^*)}\right)^2\right]$$

where

$$C_2^{\;*}(T^*) = (T^*)^2 \frac{d^2 C^*(T^*)}{d(T^*)^2}$$

The heat capacity depends only on the third virial coefficient, and its first and second derivatives and not on any parameters that are directly related to the model used for Ar_3, such as $\varepsilon_{0,el}$. This is the reason that only results for $C_p^{\;o}$ are given in this paper.

4. THE THIRD VIRIAL COEFFICIENT OF ARGON

From a statistical mechanical point of view, the third virial coefficient of argon depends on both the two and three body interactions between/among the argon atoms. A very large number of assessments have been made of the two body Ar-Ar interaction potential. The two body potential suggested by Aziz [17] may be the most accurate Ar-Ar potential. Aziz represented the repulsive wall of the potential by an exponentially decreasing function and he represented the long-range attractive part of the potential by the dispersion terms

$$- \sum_{n=6,8,10,12,14} \frac{C_n}{R_{12}^{\,n}}$$

where the C_n are the coefficients for the various dispersion terms and R_{12} represents the separation of two argon atoms. These terms represent the induced dipole-induced dipole, etc. interactions. Each dispersion term is modified by a damping function [17,18,19] that corrects the individual terms in the expansion for charge overlap effects and the entire long range attractive potential is multiplied by a factor that corrects the entire dispersion expansion for exchange overlap [17,19]; i.e. the dispersion terms are "doubly corrected".

The Aziz potential is highly parameterized and the parameters were determined [17] by using the potential to fit a wide variety of experimental data, including bulk data such as second virial coefficients and transport properties. This potential was also used to fit spectroscopic and molecular data such as the glory structure in the total cross section and beam data. Perhaps the most impressive achievement of this potential is its ability to reproduce the vibrational-rotational spectrum of Ar_2 [20]. The Aziz potential should represent the Ar-Ar interaction very accurately.

Mas, Lotrich, and Szalewicz [21] used the Aziz potential to calculate the second virial coefficient of argon in the usual way; i.e.

$$B(T) \ = \ 2\pi No \int_0^\infty \left(1 - e^{-V_{12}(R_{12})/kT}\right) R_{12}{}^2 dR_{12}$$

where $V_{12}(R_{12})$ is taken to be the Aziz potential. Mas, et.al. [21] fit their results for B(T) to a simple functional form.

These authors also calculated the third virial coefficient of argon. The third virial coefficient can be written as a sum [21];

$$C(T) \ = \ C[2,3](T) + C[3,3](T)$$

where the term C[2,3](T) is the two body contribution to the third virial coefficient ; i.e.

$$C[2,3](T) \ = \ -\frac{8\pi^2}{3} No^2 \int_0^\infty \int_0^\infty \int_{|R_{12}-R_{13}|}^{R_{12}+R_{13}} \left(e^{-V_{12}(R_{12})/kT} - 1\right)\left(e^{-V_{23}(R_{23})/kT} - 1\right)\left(e^{-V_{13}(R_{13})/kT} - 1\right) R_{12} R_{23} R_{13} dR_{12} dR_{23} dR_{13}$$

and V_{ij} is taken to be the Aziz potential. The term C[2,2](T) is the three body nonadditive contribution to the third virial coefficient; i.e.

$$C[3,3](T) \ = \ -\frac{8\pi^2}{3} No^2 \int_0^\infty \int_0^\infty \int_{|R_{12}-R_{13}|}^{R_{12}+R_{13}} \left(e^{-V_{123}/kT} - 1\right) e^{-\{V_{12}(R_{12})+V_{13}(R_{13})+V_{23}(R_{23})\}/kT} R_{12} R_{23} R_{13} dR_{12} dR_{23} dR_{13}$$

This term was evaluated by Mas, et. al. [21] using symmetry-adapted perturbation theory (SAPT) [21,22,23]. The three body potential, V_{123}, was computed by including contributions from the dispersion, induction, and exchange nonadditivities.

Again, Mas, et. al. fit their results for C(T) to a simple functional form [21];

$$C(T) = \sum_{i=0}^{8} C_i \left(\frac{273.15K}{T} - 1 \right)^i$$

where

$C_1 = 1104.105\ 8$ $\qquad$ $C_2 = 981.802\ 40$ $\qquad$ $C_3 = 601.123\ 43$

$C_4 = -\ 211.057\ 89$ $\qquad$ $C_5 = -\ 283.562\ 51$ $\qquad$ $C_6 = 7.606\ 567\ 8$

$C_7 = -\ 178.046\ 07$ $\qquad$ $C_8 = 71.694\ 400$

This expression has been used in this paper to calculate C(T) and its derivatives which

are required to obtain results for $C_p^{\ o}$. Results are shown in the third column of Table I.

5. DISCUSSION

Experimental results for the heat capacity of Ar_3 are not available to help determine

which of the calculational procedures is most accurate. However, some sources of error

in each procedure can be partially assessed.

The accuracy of the partition function method depends on the accuracy of the model

for Ar_3 and the assumptions made in the calculational procedure. It is entirely reasonable

to assume that translation and rotation are fully excited. Thus the primary errors in the

triangular Ar_3 model are due to errors in the vibrational frequencies and errors due to the

assumption that the correction terms make essentially no contribution to the heat capac-

ity. The vibrational frequency of Ar_2 is [20] 30.68 cm^{-1}; not significantly different from

the three frequencies found [2] for Ar_3. This result is reasonable. For He_3, three body con-

tributions to the potential can usually be ignored [4,24]. Although this is not the case for

Ar_3 [2,4], the three body contributions are much less important than the two body contri-

butions [23]. Thus one would reasonably expect that the Ar_3 vibrational frequencies

would be similar to the Ar_2 vibrational frequency. Even if the reported Ar_3 frequencies

are in error by a factor of three or four, the frequencies will still be low enough so that vibration is essentially fully excited at room temperature, the result obtained in this work. The effect of ignoring the correction terms to the heat capacity should be negligible since rotation and vibration are essentially fully excited.

There are also errors in the partition function approach that occur because of the computational procedure used. Although the corrections to the vibrational-rotational energy due to anharmonic vibration, non-rigid rotation, and vibration-rotation coupling have not been included in these calculations, these corrections, even if included, do not accurately represent the energy levels at high values of the vibrational (v) and rotational (j) quantum numbers [11-14]. Since the energy levels get closer together as v and j increase, the density of states increases for high v, j so that, even though the Boltzmann distribution "favors" lower values of v,j, there is a significant contribution to the thermodynamic properties from high v,j states at high temperatures leading to errors [12] in the partition function approach to the calculation of thermodynamic properties. In addition, the partition function approach does not usually allow for a sum over the continuum states that are important at high temperatures. Calculations [25] for O_2 suggest that this can lead to an error in thermodynamic properties of about 10% in high temperatures.

The errors in the cluster approach to calculating C_p^o depend entirely on the errors in the calculation of C(T), and its derivatives, which depend on the errors in the two body potential, V_{ij}, taken to be the Aziz potential [17], and the error in the three body potential, V_{123} [23]. It is difficult to assess the accuracy of V_{123}. Lotrich and Szalewicz [21,23] included the dispersion nonadditivity through fourth order, the induction nonadditivity, and the second order exchange nonadditivity. This is a substantial calculation but, since it is a

perturbation calculation, higher order terms are missing and may be important, particularly when, as in these calculations, accurate first and second derivatives of C(T) are required.

The error in V_{ij} is more important since the nonadditivity term, C[3,3](T), makes a rather minor contribution [23] to C(T). Although this two body Ar_2 potential has been tested by Aziz [17] by fitting a great deal of molecular and bulk data, and then "retested" by reproducing the experimental vibration-rotation spectrum [20] of Ar_2, it may not be satisfactory for calculating thermodynamic properties. The heat capacity of Ar_2 depends [10,14,26,27] on the second virial coefficient for Ar_2, B(T), and its first and second derivatives. Calculations of B(T) and its derivatives, using the Aziz potential, lead [27] to results for the thermodynamic properties of Ar_2 that are incorrect at lower temperatures. A similar result was obtained for [10] N_2 and for [26] O_2, using a different two body potential. These results strongly suggest that an extremely accurate two body potential, as a function of temperature, is required to obtain sufficient accuracy for the virial coefficients and their derivatives to accurately determine thermodynamic properties at lower temperatures.

The results in the third column of Table I strongly suggest that even the carefully determined results for C(T) may not be accurate enough to rigorously determine the heat capacity of Ar_3. Below 1000K, C_p^o does not continuously increase with T; a similar result was obtained in previous calculations [10,26,27]. The most likely reason for this is the need for even greater accuracy in the determination of C(T) for Ar_3.

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Table I. The Heat Capacity, C_p^o, of Ar_3 in J/mol/K

T(K)	Partition Function Method	Virial Coefficient Method
200	53.86	37.10
300	55.23	49.42
400	55.94	49.37
500	56.38	47.41
600	56.68	45.82
700	56.89	44.81
800	57.05	44.20
900	57.18	43.86
1000	57.28	43.69
2000	57.74	44.04
3000	57.89	44.59
4000	57.97	44.93
5000	58.02	45.14